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**PATENT COOPERATION TREATY (PCT)**  
**TRAITÉ DE COOPÉRATION EN MATIÈRE DE BREVETS (PCT)**

**CERTIFIED COPY OF THE INTERNATIONAL APPLICATION AS FILED  
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International Application No. }  
Demande internationale n° } **PCT/IB02/03392**

International Filing Date } **20 August 2002**  
Date du dépôt international } **(20.08.02)**

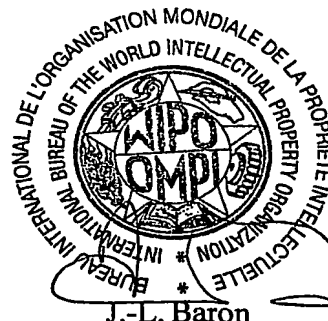
Geneva/Genève,

**26 November 2003**  
**(26.11.03)**

**International Bureau of the  
World Intellectual Property Organization (WIPO)**

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J.-L. Baron

Head, PCT Receiving Office Section  
Chef de la section "office récepteur du PCT"

## PCT

## REQUEST

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty.

For receiving Office use only

PCT/IB 02 / 03392  
International Application No.

20 AUGUST 2002  
International Filing Date 20.08.02

INTERNATIONAL BUREAU OF WIPO  
PCT International Application  
Name of receiving Office and "PCT International Application"

Applicant's or agent's file reference  
(if desired) (12 characters maximum) MOL0667-X

**Box No. I TITLE OF INVENTION**  
NON-CARBON ANODES FOR ALUMINIUM ELECTROWINNING AND OTHER OXIDATION  
RESISTANT COMPONENTS WITH IRON OXIDE-CONTAINING COATINGS

**Box No. II APPLICANT** ☐ This person is also inventor

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

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Teleprinter No.

Applicant's registration No. with the Office

State (that is, country) of nationality:

LU

State (that is, country) of residence:

LU

This person is applicant  
for the purposes of:☐ all designated  
States☒ all designated States except  
the United States of America☐ the United States  
of America only☐ the States indicated in  
the Supplemental Box

**Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)**

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

NGUYEN, Thinh T.  
Rte du Grand-lancy 165b  
1213 ONEX  
SWITZERLAND

This person is:

☐ applicant only☒ applicant and inventor☐ inventor only (If this check-box  
is marked, do not fill in below.)

Applicant's registration No. with the Office

State (that is, country) of nationality:

CH

State (that is, country) of residence:

CH

This person is applicant  
for the purposes of:☐ all designated  
States☐ all designated States except  
the United States of America☒ the United States  
of America only☐ the States indicated in  
the Supplemental Box

☐ Further applicants and/or (further) inventors are indicated on a continuation sheet.

**Box No. IV AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE**

The person identified below is hereby/has been appointed to act on behalf  
of the applicant(s) before the competent International Authorities as:

☒ agent☐ common  
representative

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)

CRONIN, Brian  
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Agent's registration No. with the Office

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☐ Address for correspondence: Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.

<b>Continuation of Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)</b> <i>If none of the following sub-boxes is used, this sheet should not be included in the request.</i>	
Name and address: <i>(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)</i>  DE NORA, Vittorio Sandrigham House NASSAU BAHAMAS	This person is: <input type="checkbox"/> applicant only <input checked="" type="checkbox"/> applicant and inventor <input type="checkbox"/> inventor only <i>(If this check-box is marked, do not fill in below.)</i> <hr/> Applicant's registration No. with the Office
State <i>(that is, country)</i> of nationality: IT	State <i>(that is, country)</i> of residence: BS
This person is applicant for the purposes of: <input type="checkbox"/> all designated States <input type="checkbox"/> all designated States except the United States of America <input checked="" type="checkbox"/> the United States of America only <input type="checkbox"/> the States indicated in the Supplemental Box	
Name and address: <i>(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)</i>  	This person is: <input type="checkbox"/> applicant only <input type="checkbox"/> applicant and inventor <input type="checkbox"/> inventor only <i>(If this check-box is marked, do not fill in below.)</i> <hr/> Applicant's registration No. with the Office
State <i>(that is, country)</i> of nationality:	State <i>(that is, country)</i> of residence:
This person is applicant for the purposes of: <input type="checkbox"/> all designated States <input type="checkbox"/> all designated States except the United States of America <input type="checkbox"/> the United States of America only <input type="checkbox"/> the States indicated in the Supplemental Box	
Name and address: <i>(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)</i>  	This person is: <input type="checkbox"/> applicant only <input type="checkbox"/> applicant and inventor <input type="checkbox"/> inventor only <i>(If this check-box is marked, do not fill in below.)</i> <hr/> Applicant's registration No. with the Office
State <i>(that is, country)</i> of nationality:	State <i>(that is, country)</i> of residence:
This person is applicant for the purposes of: <input type="checkbox"/> all designated States <input type="checkbox"/> all designated States except the United States of America <input type="checkbox"/> the United States of America only <input type="checkbox"/> the States indicated in the Supplemental Box	
Name and address: <i>(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)</i>  	This person is: <input type="checkbox"/> applicant only <input type="checkbox"/> applicant and inventor <input type="checkbox"/> inventor only <i>(If this check-box is marked, do not fill in below.)</i> <hr/> Applicant's registration No. with the Office
State <i>(that is, country)</i> of nationality:	State <i>(that is, country)</i> of residence:
This person is applicant for the purposes of: <input type="checkbox"/> all designated States <input type="checkbox"/> all designated States except the United States of America <input type="checkbox"/> the United States of America only <input type="checkbox"/> the States indicated in the Supplemental Box	
Name and address: <i>(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)</i>  	This person is: <input type="checkbox"/> applicant only <input type="checkbox"/> applicant and inventor <input type="checkbox"/> inventor only <i>(If this check-box is marked, do not fill in below.)</i> <hr/> Applicant's registration No. with the Office
State <i>(that is, country)</i> of nationality:	State <i>(that is, country)</i> of residence:
This person is applicant for the purposes of: <input type="checkbox"/> all designated States <input type="checkbox"/> all designated States except the United States of America <input type="checkbox"/> the United States of America only <input type="checkbox"/> the States indicated in the Supplemental Box	
<input type="checkbox"/> Further applicants and/or (further) inventors are indicated on another continuation sheet.	

**Box No. V DESIGNATION OF STATES***Mark the applicable check-boxes below; at least one must be marked.*

The following designations are hereby made under Rule 4.9(a):

**Regional Patent**

- ☒ **AP ARIPO Patent:** GH Ghana, GM Gambia, KE Kenya, LS Lesotho, MW Malawi, MZ Mozambique, SD Sudan, SL Sierra Leone, SZ Swaziland, TZ United Republic of Tanzania, UG Uganda, ZM Zambia, ZW Zimbabwe, and any other State which is a Contracting State of the Harare Protocol and of the PCT (*if other kind of protection or treatment desired, specify on dotted line*) .....
- ☒ **EA Eurasian Patent:** AM Armenia, AZ Azerbaijan, BY Belarus, KG Kyrgyzstan, KZ Kazakhstan, MD Republic of Moldova, RU Russian Federation, TJ Tajikistan, TM Turkmenistan, and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT
- ☒ **EP European Patent:** AT Austria, BE Belgium, BG Bulgaria, CH & LI Switzerland and Liechtenstein, CY Cyprus, CZ Czech Republic, DE Germany, DK Denmark, EE Estonia, ES Spain, FI Finland, FR France, GB United Kingdom, GR Greece, IE Ireland, IT Italy, LU Luxembourg, MC Monaco, NL Netherlands, PT Portugal, SE Sweden, SK Slovakia, TR Turkey, and any other State which is a Contracting State of the European Patent Convention and of the PCT
- ☐ **OA OAPI Patent:** BF Burkina Faso, BJ Benin, CF Central African Republic, CG Congo, CI Côte d'Ivoire, CM Cameroon, GA Gabon, GN Guinea, GQ Equatorial Guinea, GW Guinea-Bissau, ML Mali, MR Mauritania, NE Niger, SN Senegal, TD Chad, TG Togo, and any other State which is a member State of OAPI and a Contracting State of the PCT (*if other kind of protection or treatment desired, specify on dotted line*) .....

**National Patent** (*if other kind of protection or treatment desired, specify on dotted line*):

- |   |  |   |
|---|--|---|
| <input type="checkbox"/> AE United Arab Emirates .....                          | <input type="checkbox"/> GM Gambia .....   | <input checked="" type="checkbox"/> NZ New Zealand .....              |
| <input type="checkbox"/> AG Antigua and Barbuda .....                           | <input type="checkbox"/> HR Croatia .....  | <input type="checkbox"/> OM Oman .....                                |
| <input type="checkbox"/> AL Albania .....                                       | <input checked="" type="checkbox"/> HU Hungary .....                               | <input type="checkbox"/> PH Philippines .....                         |
| <input type="checkbox"/> AM Armenia .....                                       | <input checked="" type="checkbox"/> ID Indonesia .....                             | <input checked="" type="checkbox"/> PL Poland .....                   |
| <input checked="" type="checkbox"/> AT Austria .....                            | <input type="checkbox"/> IL Israel .....   | <input type="checkbox"/> PT Portugal .....                            |
| <input checked="" type="checkbox"/> AU Australia .....                          | <input checked="" type="checkbox"/> IN India .....                                 | <input checked="" type="checkbox"/> RO Romania .....                  |
| <input type="checkbox"/> AZ Azerbaijan .....                                    | <input checked="" type="checkbox"/> IS Iceland .....                               | <input checked="" type="checkbox"/> RU Russian Federation .....       |
| <input type="checkbox"/> BA Bosnia and Herzegovina .....                        | <input checked="" type="checkbox"/> JP Japan .....                                 | <input type="checkbox"/> SD Sudan .....                               |
| <input type="checkbox"/> BB Barbados .....                                      | <input type="checkbox"/> KE Kenya .....  | <input checked="" type="checkbox"/> SE Sweden .....                   |
| <input type="checkbox"/> BG Bulgaria .....                                      | <input type="checkbox"/> KG Kyrgyzstan .....                                       | <input type="checkbox"/> SG Singapore .....                           |
| <input checked="" type="checkbox"/> BR Brazil .....                             | <input checked="" type="checkbox"/> KP Democratic People's Republic of Korea ..... | <input checked="" type="checkbox"/> SI Slovenia .....                 |
| <input type="checkbox"/> BY Belarus .....                                       | <input checked="" type="checkbox"/> KR Republic of Korea .....                     | <input checked="" type="checkbox"/> SK Slovakia .....                 |
| <input type="checkbox"/> BZ Belize .....  | <input type="checkbox"/> KZ Kazakhstan .....                                       | <input type="checkbox"/> SL Sierra Leone .....                        |
| <input checked="" type="checkbox"/> CA Canada .....                             | <input type="checkbox"/> LC Saint Lucia .....                                      | <input checked="" type="checkbox"/> TJ Tajikistan .....               |
| <input checked="" type="checkbox"/> CH & LI Switzerland and Liechtenstein ..... | <input type="checkbox"/> LK Sri Lanka .....  | <input type="checkbox"/> TM Turkmenistan .....                        |
| <input checked="" type="checkbox"/> CN China .....                              | <input type="checkbox"/> LR Liberia .....  | <input type="checkbox"/> TN Tunisia .....                             |
| <input type="checkbox"/> CO Colombia .....                                      | <input type="checkbox"/> LS Lesotho .....  | <input checked="" type="checkbox"/> TR Turkey .....                   |
| <input type="checkbox"/> CR Costa Rica .....                                    | <input type="checkbox"/> LT Lithuania .....  | <input type="checkbox"/> TT Trinidad and Tobago .....                 |
| <input type="checkbox"/> CU Cuba .....  | <input type="checkbox"/> LU Luxembourg .....                                       | <input type="checkbox"/> TZ United Republic of Tanzania .....         |
| <input checked="" type="checkbox"/> CZ Czech Republic .....                     | <input type="checkbox"/> LV Latvia .....   | <input checked="" type="checkbox"/> UA Ukraine .....                  |
| <input checked="" type="checkbox"/> DE Germany .....                            | <input type="checkbox"/> MA Morocco .....  | <input type="checkbox"/> UG Uganda .....                              |
| <input checked="" type="checkbox"/> DK Denmark .....                            | <input type="checkbox"/> MD Republic of Moldova .....                              | <input checked="" type="checkbox"/> US United States of America ..... |
| <input type="checkbox"/> DM Dominica .....                                      | <input type="checkbox"/> MG Madagascar .....                                       | <input type="checkbox"/> UZ Uzbekistan .....                          |
| <input type="checkbox"/> DZ Algeria .....                                       | <input type="checkbox"/> MK The former Yugoslav Republic of Macedonia .....        | <input type="checkbox"/> VN Viet Nam .....                            |
| <input type="checkbox"/> EC Ecuador .....                                       | <input type="checkbox"/> MN Mongolia .....   | <input checked="" type="checkbox"/> YU Yugoslavia .....               |
| <input type="checkbox"/> EE Estonia .....                                       | <input type="checkbox"/> MW Malawi .....   | <input checked="" type="checkbox"/> ZA South Africa .....             |
| <input checked="" type="checkbox"/> ES Spain .....                              | <input checked="" type="checkbox"/> MX Mexico .....                                | <input type="checkbox"/> ZM Zambia .....                              |
| <input checked="" type="checkbox"/> FI Finland .....                            | <input type="checkbox"/> MZ Mozambique .....                                       | <input type="checkbox"/> ZW Zimbabwe .....                            |
| <input checked="" type="checkbox"/> GB United Kingdom .....                     | <input checked="" type="checkbox"/> NO Norway .....                                |   |
| <input type="checkbox"/> GD Grenada .....                                       |  |   |
| <input type="checkbox"/> GE Georgia .....                                       |  |   |
| <input type="checkbox"/> GH Ghana .....   |  |   |

Check-boxes below reserved for designating States which have become party to the PCT after issuance of this sheet:

- |                                |                                |                                |
|--------------------------------|--------------------------------|--------------------------------|
| <input type="checkbox"/> ..... | <input type="checkbox"/> ..... | <input type="checkbox"/> ..... |
| <input type="checkbox"/> ..... | <input type="checkbox"/> ..... | <input type="checkbox"/> ..... |

**Precautionary Designation Statement:** In addition to the designations made above, the applicant also makes under Rule 4.9(b) all other designations which would be permitted under the PCT except any designation(s) indicated in the Supplemental Box as being excluded from the scope of this statement. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit. (*Confirmation (including fees) must reach the receiving Office within the 15-month time limit.*)

**Box No. VI PRIORITY CLAIM**

The priority of the following earlier application(s) is hereby claimed:

Filing date of earlier application (day/month/year)	Number of earlier application	Where earlier application is:		
		national application: country or Member of WTO	regional application:* regional Office	international application: receiving Office
item (1)				
item (2)				
item (3)				
item (4)				
item (5)				

☐ Further priority claims are indicated in the Supplemental Box.

The receiving Office is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) (only if the earlier application was filed with the Office which for the purposes of this international application is the receiving Office) identified above as:

☐ all items    ☐ item (1)    ☐ item (2)    ☐ item (3)    ☐ item (4)    ☐ item (5)    ☐ other, see Supplemental Box

\* Where the earlier application is an ARIPO application, indicate at least one country party to the Paris Convention for the Protection of Industrial Property or one Member of the World Trade Organization for which that earlier application was filed (Rule 4.10(b)(ii)): . . . .

**Box No. VII INTERNATIONAL SEARCHING AUTHORITY**

Choice of International Searching Authority (ISA) (if two or more International Searching Authorities are competent to carry out the international search, indicate the Authority chosen; the two-letter code may be used):

ISA / EP

Request to use results of earlier search; reference to that search (if an earlier search has been carried out by or requested from the International Searching Authority):

Date (day/month/year)

Number

Country (or regional Office)

**Box No. VIII DECLARATIONS**

The following declarations are contained in Boxes Nos. VIII (i) to (v) (mark the applicable check-boxes below and indicate in the right column the number of each type of declaration):

Number of  
declarations

- |   |  |   |
|---|--|---|
| <input type="checkbox"/> Box No. VIII (i)   | Declaration as to the identity of the inventor   | : |
| <input type="checkbox"/> Box No. VIII (ii)  | Declaration as to the applicant's entitlement, as at the international filing date, to apply for and be granted a patent             | : |
| <input type="checkbox"/> Box No. VIII (iii) | Declaration as to the applicant's entitlement, as at the international filing date, to claim the priority of the earlier application | : |
| <input type="checkbox"/> Box No. VIII (iv)  | Declaration of inventorship (only for the purposes of the designation of the United States of America)                               | : |
| <input type="checkbox"/> Box No. VIII (v)   | Declaration as to non-prejudicial disclosures or exceptions to lack of novelty   | : |

**Box No. IX CHECK LIST; LANGUAGE OF FILING**

This international application contains:

(a) the following number of sheets in paper form:

request (including declaration sheets) : 5  
 description (excluding sequence listing part) : 14  
 claims : 6  
 abstract : 1  
 drawings : \_\_\_\_\_

Sub-total number of sheets : 26

sequence listing part of description (actual number of sheets if filed in paper form, whether or not also filed in computer readable form; see (b) below) : \_\_\_\_\_

Total number of sheets : 26

(b) sequence listing part of description filed in computer readable form

(i) ☐ only (under Section 801(a)(i))(ii) ☐ in addition to being filed in paper form (under Section 801(a)(ii))

Type and number of carriers (diskette, CD-ROM, CD-R or other) on which the sequence listing part is contained (additional copies to be indicated under item 9(ii), in right column): .....

This international application is accompanied by the following item(s) (mark the applicable check-boxes below and indicate in right column the number of each item):

Number of items

1. ☐ fee calculation sheet :
2. ☐ original separate power of attorney :
3. ☐ original general power of attorney :
4. ☐ copy of general power of attorney; reference number, if any: ..... :
5. ☐ statement explaining lack of signature :
6. ☐ priority document(s) identified in Box No. VI as item(s): ..... :
7. ☐ translation of international application into (language): ..... :
8. ☐ separate indications concerning deposited microorganism or other biological material :
9. ☐ sequence listing in computer readable form (indicate also type and number of carriers (diskette, CD-ROM, CD-R or other))
  - (i) ☐ copy submitted for the purposes of international search under Rule 13ter only (and not as part of the international application) :
  - (ii) ☐ (only where check-box (b)(i) or (b)(ii) is marked in left column) additional copies including, where applicable, the copy for the purposes of international search under Rule 13ter :
  - (iii) ☐ together with relevant statement as to the identity of the copy or copies with the sequence listing part mentioned in left column :
10. ☐ other (specify): ..... :

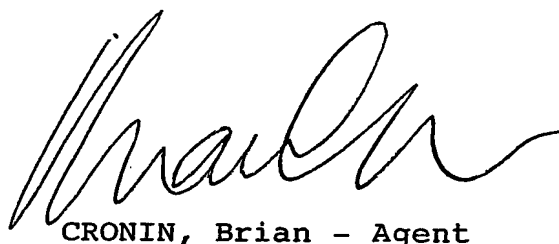
Figure of the drawings which should accompany the abstract:

Language of filing of the international application:

English

**Box No. X SIGNATURE OF APPLICANT, AGENT OR COMMON REPRESENTATIVE**

Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the request).



CRONIN, Brian - Agent

For receiving Office use only

1. Date of actual receipt of the purported international application:

20 AUGUST 2002

(20.08.02)

3. Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application:

4. Date of timely receipt of the required corrections under PCT Article 11(2):

5. International Searching Authority (if two or more are competent): ISA /

6. ☐ Transmittal of search copy delayed until search fee is paid

2. Drawings:

☐ received:☐ not received:

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Date of receipt of the record copy by the International Bureau:

NON-CARBON ANODES FOR ALUMINIUM ELECTROWINNING  
AND OTHER OXIDATION RESISTANT COMPONENTS  
WITH IRON OXIDE-CONTAINING COATINGS

Field of the Invention

This invention relates to a method of manufacturing non-carbon anodes for use in aluminium electrowinning cells as well as other oxidation resistant components.

5

Background Art

Using non-carbon anodes for the electrowinning of aluminium should drastically improve the aluminium production process by reducing pollution and the cost of aluminium production. Many attempts have been made to use  
10 oxide anodes, cermet anodes and metal-based anodes for aluminium production, however they were never adopted by the aluminium industry.

For the dissolution of the raw material, usually alumina, a highly aggressive fluoride-based electrolyte,  
15 such as cryolite, is required.

The materials having the greatest resistance to oxidation are metal oxides which are all to some extent soluble in cryolite. Oxides are also poorly electrically conductive, therefore, to avoid substantial ohmic losses  
20 and high cell voltages, the use of oxides should be minimal in the manufacture of anodes. Whenever possible, a good conductive material should be utilised for the anode core, whereas the surface of the anode is preferably made of an oxide having a high  
25 electrocatalytic activity.

Several patents disclose the use of an electrically conductive metal anode core with an oxide-based active outer part, in particular US patents 4,956,069, 4,960,494, 5,069,771 (all Nguyen/Lazouni/Doan), 6,077,415  
30 (Duruz/de Nora), 6,103,090 (de Nora), 6,113,758 (de Nora/Duruz) and 6,248,227 (de Nora/Duruz), as well as PCT publications WO00/06803 (Duruz/de Nora/Crottaz),

- 2 -

WO00/06804 (Crottaz/Duruz), WO00/40783 (de Nora/Duruz),  
WO01/42534 (de Nora/Duruz) and WO01/42536 (Nguyen/Duruz/  
de Nora).

5 US patents 4,039,401 and 4,173,518 (both Yamada/  
Hashimoto/Horinouchi) disclose multiple oxides for use as  
electrochemically active anode material for aluminium  
electrowinning. The multiple oxides include inter-alia  
oxides of iron, nickel, titanium and yttrium, such as  
10  $\text{NiFe}_2\text{O}_4$  or  $\text{TiFe}_2\text{O}_4$ , in the '401 patent, and oxides of  
yttrium, iron, titanium and tantalum, such as  $\text{Fe}_2\text{O}_3 \cdot \text{Ta}_2\text{O}_5$ ,  
in the '518 patent. The multiple oxides are produced by  
sintering their constitutive single oxides and then they  
are crushed and applied onto a metal substrate (titanium,  
nickel or copper) by spraying or dipping. Alternatively,  
15 the multiple oxides can be produced by electroplating  
onto the metal substrate the constitutive metals of the  
multiple oxides followed by an oxidation treatment.

Likewise US patents 4,374,050 and 4,374,761 (both  
Ray) disclose non-stoichiometric multiple oxides for use  
20 as electrochemically active anode material for aluminium  
electrowinning. The multiple oxides include inter-alia  
oxides of nickel, titanium, tantalum, yttrium and iron,  
in particular nickel-iron oxides. The multiple oxides are  
produced by sintering their constitutive single oxides  
25 and then they can be clad onto a metal substrate.

WO99/36591 (de Nora), WO99/36593 and WO99/36594  
(both Duruz/de Nora) disclose sintered multiple oxide  
coatings applied onto a metal substrate from a slurry  
containing particulate of the multiple oxides in a  
30 colloidal and/or inorganic polymeric binder, in  
particular colloidal or polymeric alumina, ceria, lithia,  
magnesia, silica, thoria, yttria, zirconia, tin oxide or  
zinc oxide. The multiple oxides include ferrites of  
cobalt, copper, chromium, manganese, nickel and zinc. It  
35 is mentioned that the coating can be obtained by reacting  
precursors thereof among themselves or with constituents  
of the substrate.

US patent 6,372,119 and WO01/31091 (both Ray/Liu/  
Weirauch) disclose a cermet made from sintered particles  
40 of nickel, iron and cobalt oxides and of metallic copper



and silver possibly alloyed with cobalt, nickel, iron, aluminium, tin, niobium, tantalum, chromium molybdenum or tungsten. The particles can be applied as a coating onto an anode substrate and sintered thereon to form an anode for the electrowinning of aluminium.

These non-carbon anodes have not as yet been commercially and industrially applied and there is still a need for metal-based anodes for aluminium production.

#### Summary of the Invention

The present invention relates to a method of forming a dense and crack-free hematite-containing protective layer on a metal-based substrate, in particular a metallic substrate, for use in a high temperature oxidising and/or corrosive environment. The method comprises: (I) applying onto the substrate a particle mixture comprising particles of hematite ( $\text{Fe}_2\text{O}_3$ ) and particles of: (a) iron metal (Fe) with a weight ratio  $\text{Fe}/\text{Fe}_2\text{O}_3$  of at least 0.3 and preferably below 2, in particular in the range from 0.8 to 1.4; or (b) ferrous oxide ( $\text{FeO}$ ) with a weight ratio  $\text{FeO}/\text{Fe}_2\text{O}_3$  of at least 0.35 and preferably below 2.5, in particular in the range from 0.9 to 1.7; or (c) iron metal (Fe) and ferrous oxide ( $\text{FeO}$ ), with weight ratios  $\text{Fe}/\text{Fe}_2\text{O}_3$  and  $\text{FeO}/\text{Fe}_2\text{O}_3$  that are in pro rata with the ratios of (a) and (b); and (II) consolidating the applied particle mixture to form the hematite-containing protective layer by heat treating the particle mixture to: 1) oxidise when present the iron metal (Fe) into ferrous oxide ( $\text{FeO}$ ); 2) sinter the hematite particles to form a porous sintered hematite matrix; and 3) oxidise into hematite ( $\text{Fe}_2\text{O}_3$ ) the ferrous oxide ( $\text{FeO}$ ) present in the mixture as such and/or in the form of the oxidised iron metal, to fill the sintered hematite matrix.

The formation of hematite from the ferrous oxide results in a volume expansion such that it fills the porous sintered hematite matrix and inhibits formation of cracks by contraction of the pores of the hematite matrix during sintering. The method thus provides a hematite-containing protective layer that is dense and substantially crack-free and that inhibits diffusion from

and to the metal-based substrate, in particular it prevents diffusion of constituents, such as nickel, from the substrate.

It has been observed that when the weight ratio Fe/Fe<sub>2</sub>O<sub>3</sub> is at 0.3, 90% of the contraction cracks in the protective layer can be eliminated compared to a layer produced from a mixture which does not contain metallic iron. When the weight ratio Fe/Fe<sub>2</sub>O<sub>3</sub> is at or above 0.75 or 0.8, all contraction cracks can be eliminated. Above a weight ratio of 1.4 or 1.5, the protective layer is still dense and crack-free, however a satisfactory oxidation of Fe and FeO into Fe<sub>2</sub>O<sub>3</sub>, i.e. without significant incomplete oxidation of Fe/FeO into Fe<sub>2</sub>O<sub>3</sub>, is more difficult to achieve even though it is still possible. Above a weight ratio Fe/Fe<sub>2</sub>O<sub>3</sub> of 2, a satisfactory oxidation of Fe and FeO into Fe<sub>2</sub>O<sub>3</sub> is even more difficult to obtain. Such a high Fe concentration can nevertheless be contemplated for applications for which the presence of incompletely oxidised iron in the protective layer is not detrimental. The same considerations apply of course equally to the presence of FeO or a combination of Fe and FeO in the particle mixture.

Best results have been obtained with starting compositions of the particle mixture having a weight ratio Fe/Fe<sub>2</sub>O<sub>3</sub> from 1 to 1.2 or a weight ratio FeO/Fe<sub>2</sub>O<sub>3</sub> from 1.45 to 1.8 or, when both Fe and FeO are used in the particle mixture, a pro rata combination thereof.

The protective layer should contain sufficient iron oxide to form a sintered iron oxide matrix that possibly contains minor amounts of further elements, such as additives, dopants and catalysts. Usually, the layer contains at least 50 weight% iron oxide, typically at least 75 weight% oxide and preferably at least 85 weight or even at least 90 weight%.

The electrical/electrochemical properties of the protective layer can be improved with additives, such as oxides of titanium, yttrium, ytterbium, tantalum, manganese, zinc, zirconium, cerium and nickel and/or heat-convertible precursors thereof. The additive(s) can be present in the protective layer in a total amount of 1

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to 50 weight%. Usually, it is sufficient for the additive(s) to be present in a catalytic amount to achieve the electrical/electrochemical effect, in particular in a total amount of 1 to 30 weight% or even 5 to 15 weight%. Limiting the amount of additives also reduces the risk of contamination of the protective layer's environment during use, e.g. an electrolyte of a metal electrowinning cell.

The protective layer can further comprise at least one metal selected from Cu, Ag, Pd, Pt, Co, Cr, Al, Ga, Ge, Hf, In, Ir, Mo, Mn, Nb, Os, Re, Rh, Ru, Se, Si, Sn, Ti, V, W, Li, Ca, Ce and Nb and/or an oxide thereof which can be added to the particle mixture as such, e.g. as particles, or as a precursor, e.g. as particles or in solution, for example a salt such as a chloride, sulfate, nitrate, chlorate or perchlorate, or a metal organic compound such as an alkoxide, formate or acetate. Such a metal and/or oxide can be present in the protective layer in a total amount of 1 to 15 weight%, preferably from 1 to 5 or 10 weight%.

Minor amounts of copper or copper oxides, i.e. up to 5 or 10 weight%, improve the electrical conductivity of the protective layer and diffusion of iron oxide (and possibly other oxides) during the sintering of the protective layer. This leads to the production of more conductive and denser protective layers than without the use of copper metal and/or oxides.

The particle mixture can be made of particles that are smaller than 75 micron, preferably smaller than 50 micron, in particular from 5 to 45 micron.

The metal-based substrate can be metallic, ceramic, a cermet or a surface-oxidised metal.

Usually, the metal-based substrate comprises at least one metal selected from chromium, cobalt, hafnium, iron, molybdenum, nickel, copper, niobium, platinum, silicon, tantalum, titanium, tungsten, vanadium, yttrium and zirconium or an oxide thereof. For instance, the metal-based substrate comprises an alloy of iron, in particular an iron alloy containing nickel and/or cobalt.

Advantageously, the method of the invention comprises oxidising the surface of a metallic substrate to form an integral anchorage layer thereon to which the protective layer is bonded by sintering during heat treatment, in particular an integral layer containing an oxide of iron and/or another metal, such as nickel, that is sintered during the heat treatment with iron oxide from the particle mixture. Further details on such an anchoring of the protective layer are disclosed in PCT/IB02/01239 (Nguyen/de Nora).

When used for aluminium electrowinning, the protected metal-based substrate preferably contains at least one metal selected from nickel, iron, cobalt, copper, aluminium and yttrium. Suitable alloys for such a metal-based substrate are disclosed in US Patent 6,372,099 (Duruz/de Nora), and WO00/06803 (Duruz/de Nora/Crottaz), WO00/06804 (Crottaz/Duruz), WO01/42534 (de Nora/Duruz), WO01/42536 (Duruz/Nguyen/de Nora), PCT/IB01/01241 (Nguyen/de Nora), PCT/IB01/01838 (Nguyen/Duruz/de Nora) and PCT/IB02/00820 (Nguyen/de Nora).

The particle mixture can be applied onto the substrate as a slurry. Such a slurry may comprise an organic binder which is at least partly volatilised during sintering, in particular a binder selected from polyvinyl alcohol, polyvinyl acetate, polyacrylic acid, hydroxy propyl methyl cellulose, polyethylene glycol, ethylene glycol, hexanol, butyl benzyl phthalate and ammonium polymethacrylate. The slurry may also comprise an inorganic binder, in particular a colloid, such as a colloid selected from lithia, beryllium oxide, magnesia, alumina, silica, titania, vanadium oxide, chromium oxide, manganese oxide, iron oxide, gallium oxide, yttria, zirconia, niobium oxide, molybdenum oxide, ruthenia, indium oxide, tin oxide, tantalum oxide, tungsten oxide, thallium oxide, ceria, hafnia and thoria, and precursors thereof such as hydroxides, nitrates, acetates and formates thereof, all in the form of colloids; and/or an inorganic polymer, such as a polymer selected from lithia, beryllium oxide, alumina, silica, titania, chromium oxide, iron oxide, nickel oxide, gallium oxide,

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zirconia, niobium oxide, ruthenia, indium oxide, tin oxide, hafnia, tantalum oxide, ceria and thorium, and precursors thereof such as hydroxides, nitrates, acetates and formates thereof, all in the form of inorganic polymers. Such an inorganic binder may be sintered during the heat treatment with an oxide of an anchorage layer which is integral with the metal-based substrate to bind the protective layer to the metal-based substrate.

Typically, the particle mixture is consolidated on the substrate by heat treatment at a temperature in the range from 800° to 1400°C, in particular from 850° to 1150°C. The particle mixture can be consolidated on the substrate by heat treatment for 1 to 48 hours, in particular for 5 to 24 hours. Usually, the particle mixture is consolidated on the substrate by heat treatment in an atmosphere containing 10 to 100 mol% O<sub>2</sub>.

Further details on the application of inorganic colloidal and/or polymeric slurries on metal substrates are disclosed in US Patents 6,361,681 (de Nora/Duruz) and 6,365,018 (de Nora) and in PCT/IB02/01239 (Nguyen/de Nora).

Typically, the component of the invention is a component of a cell for the electrowinning of a metal such as aluminium, in particular a current carrying anodic component such as an active anode structure or an anode stem, or another cell component exposed to molten electrolyte and/or cell fumes, such as a cell cover or a powder feeder. Examples of such cell components are disclosed in WO00/40781 and WO00/40782 (both de Nora), WO00/63464 (de Nora/Berclaz), WO01/31088 (de Nora) and PCT/IB02/00669 (de Nora/Berclaz). The applied layers on such cell components can be consolidated before use by heat treating the components over a cell.

Advantageously, the particle mixture can be consolidated by heat treating the cell component over the cell to form the protective layer. By carrying out the consolidation heat-treatment immediately before use, thermal shocks and stress caused by cooling and reheating of the component between consolidation and use can be avoided.

Another aspect of the invention relates to a method of electrowinning a metal such as aluminium. The method comprises manufacturing by the above described method a current-carrying anodic component protected by a protective layer, installing the anodic component in a molten electrolyte containing a dissolved salt of the metal to electrowin, such as alumina, and passing an electrolysis current from the anodic component to a facing cathode in the molten electrolyte to evolve oxygen anodically and produce the metal cathodically.

The electrolyte can be a fluoride-based molten electrolyte, in particular containing fluorides of aluminium and sodium. Further details of suitable electrolyte compositions are for example disclosed in PCT/IB02/01952 (Nguyen/de Nora).

The cell can be operated with an electrolyte maintained at a temperature in the range from 800° to 960°C, in particular from 880° to 940°C.

Preferably, to reduce the solubility of metal-based cell components, an alumina concentration which is at or close to saturation is maintained in the electrolyte, particularly adjacent the anodic component.

An amount of iron species can also be maintained in the electrolyte to inhibit dissolution of the protective layer of the anodic component. Further details on such a cell operation are disclosed in the above mentioned US Patent 6,372,099.

The invention relates also to method of electrowinning a metal such as aluminium. The method comprises manufacturing by the above disclosed method a cover protected by a protective layer, placing the cover over a metal production cell trough containing a molten electrolyte in which a salt of the metal to electrowin is dissolved, passing an electrolysis current in the molten electrolyte to evolve oxygen anodically and metal cathodically, and confining electrolyte vapours and evolved oxygen within the cell trough by means of the protective layer of the cover.

Further features of cell covers are disclosed in US Patent 6,402,928 (de Nora/Sekhar), PCT/IB02/00669 (de Nora/Berclaz) and PCT/IB02/02018.

5 A further aspect of the invention relates to a hematite-containing protective layer on a metal-based substrate for use in a high temperature oxidising and/or corrosive environment. The protective layer on the substrate is producible by the above described method.

10 Yet a further aspect of the invention concerns a cell for the electrowinning of a metal, such as aluminium, having at least one component that comprises a metal-based substrate covered with a hematite-containing protective layer as defined above.

#### Detailed Description

15 Examples of starting compositions of particle mixtures for producing protective layers according to the invention are given in Table 1, which shows the weight percentages of the indicated constituents for each specimen A1-H1. Examples of alloy compositions of  
20 substrates for application of protective layers according to the invention are given in Table 2, which shows the weight percentages of the indicated metals for each specimen A2-O2.

TABLE 1

25

	Fe <sub>2</sub> O <sub>3</sub>	Fe	TiO <sub>2</sub>	ZrO <sub>2</sub>	ZnO	CuO
A1	47	41	10	--	--	2
B1	65	23	10	--	--	2
C1	45	45	--	10	--	--
D1	43	52	--	--	--	5
E1	55	23	10	10	--	2
F1	40	48	1	7	--	4
G1	53	35	5	--	4	3
H1	46	44	--	--	8	2

TABLE 2

	Ni	Fe	Co	Cu	Al	Y	Mn	Si	C
A2	48	38	--	10	3	--	0.5	0.45	0.05
B2	49	40	--	7	3	--	0.5	0.45	0.05
C2	36	50	--	10	3	--	0.5	0.45	0.05
D2	36	50	--	10	3	0.35	0.3	0.3	0.05
E2	36	53	--	7	3	--	0.5	0.45	0.05
F2	36	53	--	7	3	0.35	0.3	0.3	0.05
G2	48	38	--	10	3	0.35	0.3	0.3	0.05
H2	22	68	--	5.5	4	--	0.25	0.2	0.05
I2	42	42	--	12	2	1	0.5	0.45	0.05
J2	42	40	--	12.5	4	0.4	0.45	0.6	0.05
K2	45	44	--	7	3	--	0.5	0.45	0.05
L2	30	69	--	--	--	--	0.5	0.45	0.05
M2	25	65	7	1	1	--	0.5	0.45	0.05
N2	59	40	--	--	--	--	0.5	0.45	0.05
O2	50	47.4	--	--	--	1.7	0.35	0.5	0.05

Comparative Example

5        An anode was manufactured from an anode rod of diameter 20 mm and total length 20 mm made of a cast alloy having the composition of sample A2 of Table 2. The anode rod was supported by a stem made of an alloy containing nickel, chromium and iron, such as Inconel, 10        protected with an alumina sleeve. The anode was suspended for 16 hours over a molten cryolite-based electrolyte at 925°C whereby its surface was oxidised.

Electrolysis was carried out by fully immersing the anode rod in the molten electrolyte. The electrolyte



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contained 18 weight% aluminium fluoride ( $\text{AlF}_3$ ), 6.5 weight% alumina ( $\text{Al}_2\text{O}_3$ ) and 4 weight% calcium fluoride ( $\text{CaF}_2$ ), the balance being cryolite ( $\text{Na}_3\text{AlF}_6$ ).

5 The current density was about  $0.8 \text{ A/cm}^2$  and the cell voltage was at 3.5-3.8 volt throughout the test. The concentration of dissolved alumina in the electrolyte was maintained during the entire electrolysis by periodically feeding fresh alumina into the cell.

10 After 50 hours electrolysis was interrupted and the anode extracted. Upon cooling the anode was examined externally and in cross-section.

The anode's outer dimensions had remained substantially unchanged. The anode's oxide outer part had grown from an initial thickness of about 70 micron to a  
15 thickness after use of about up to 500 micron.

Samples of the used electrolyte and the product aluminium were also analysed. It was found that the electrolyte contained 150-280 ppm nickel and the product aluminium contained roughly 1000 ppm nickel.

20

#### Example 1

An aluminium electrowinning anode was prepared according to the invention as follows:

25 A slurry for coating an anode substrate was prepared by suspending in 32.5 g of an aqueous solution containing 5 weight% polyvinyl alcohol (PVA) 67.5 g of a particle mixture made of hematite  $\text{Fe}_2\text{O}_3$  particles, iron metal particles,  $\text{TiO}_2$  particles and  $\text{CuO}$  particles (with particle size of -325 mesh, i.e. smaller than 44 micron) in a weight ratio corresponding to sample A1 of Table 1.

30 An anode substrate made of the alloy of sample A2 of Table 2 was covered with ten layers of this slurry that were applied with a brush. The applied layers were dried for 10 hours at  $140^\circ\text{C}$  in air and then consolidated at  $1100^\circ\text{C}$  for 24 hours to form a protective hematite-based  
35 coating which had a thickness of 0.4 to 0.45 mm.

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During consolidation, the  $\text{Fe}_2\text{O}_3$  particles were sintered together into a porous matrix with a volume contraction. The  $\text{TiO}_2$  particles and  $\text{CuO}$  particles were dissolved in the sintered  $\text{Fe}_2\text{O}_3$ . Simultaneously, the iron  
5 metal particles were successively oxidised into  $\text{FeO}$  (ferrous oxide),  $\text{Fe}_3\text{O}_4$  (magnetite) and  $\text{Fe}_2\text{O}_3$  (hematite) with a volume expansion compensating the above volume contraction and filling the porous hematite matrix.

The formation of the hematite from the ferrous oxide  
10 resulted in a volume expansion such that the thus formed hematite filled the porous sintered hematite matrix and inhibited formation of cracks by contraction of the pores of the hematite matrix during sintering that would be formed in the absence of iron metal in the particle  
15 mixture. The hematite-containing protective layer was thus dense and crack-free and able to inhibit diffusion from and to the metal-based substrate.

Underneath the coating, an integral oxide scale mainly of iron oxide had grown from the substrate during  
20 the heat treatment and sintered with iron oxide and titanium oxide from the coating to firmly anchor the coating to the substrate. The sintered integral oxide scale contained titanium oxide in an amount of about 10 metal weight%. Minor amounts of copper, aluminium and  
25 nickel were also found in the oxide scale (less than 5 metal weight% in total).

#### Example 2

An anode was prepared as in Example 1 by covering an iron-alloy substrate with layers of a slurry containing a  
30 particle mixture of  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}$ ,  $\text{TiO}_2$  and  $\text{CuO}$ .

The applied layers were dried and then consolidated by suspending the anode for 36 hours over a cryolite-based electrolyte at about  $925^\circ\text{C}$ . The electrolyte contained 18 weight% aluminium fluoride ( $\text{AlF}_3$ ), 6.5  
35 weight% alumina ( $\text{Al}_2\text{O}_3$ ) and 4 weight% calcium fluoride ( $\text{CaF}_2$ ), the balance being cryolite ( $\text{Na}_3\text{AlF}_6$ ).

Upon consolidation of the layers, the anode was immersed in the molten electrolyte and an electrolysis

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current was passed from the anode to a facing cathode through the alumina-containing electrolyte to evolve oxygen anodically and produce aluminium cathodically. A high oxygen evolution was observed during the test. The  
5 current density was about 0.8 A/cm<sup>2</sup> and the cell voltage was stable at 3.1-3.2 volt throughout the test.

Compared to an uncoated anode, i.e. the anode the comparative Example, the coating of an alloy-anode with an oxide protective layer according to the invention led  
10 to an improvement of the anode performance such that the cell voltage was stabilised and also reduced by 0.4 to 0.6 volt, which corresponds to about 10 to 20%, thus permitting tremendous energy savings.

After 50 hours, the anode was extracted from the  
15 electrolyte and underwent cross-sectional examination.

The dimension of the coating had remained substantially unchanged. However, TiO<sub>2</sub> had selectively been dissolved in the electrolyte from the protective coating. The integral oxide layer of the anode substrate  
20 had grown to a thickness of 200 micron, i.e. at a much slower rate than the oxide layer of the uncoated anode of the Comparative Example.

Samples of the used electrolyte and the product aluminium were also analysed. It was found that the  
25 electrolyte contained less than 70 ppm nickel and the produced aluminium contained less than 300 ppm nickel which is significantly lower than with the uncoated anode of the Comparative Example. This demonstrated that the protective coating of the invention constituted an  
30 efficient barrier reducing nickel dissolution from the anode's alloy inhibiting contamination of the product aluminium by nickel.

### Example 3

Examples 1 and 2 can be repeated using different  
35 combinations of coating compositions (A1-H1) selected from Table 1 and metal alloy compositions (A2-O2) selected from Table 2.

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While the invention has been described in conjunction with specific embodiments thereof, it is evident that alternatives, modifications, and variations will be apparent to those skilled in the art.

- 5        For example, in a modification of the invention, all the materials described above for forming the hematite-containing protective layers can alternatively be shaped into a body and sintered to form a massive component, in particular an aluminium electrowinning anode, made of the
- 10 hematite-containing material. Such a component can be made of oxides or, especially when used as a current carrying component, of a cermet having a metal phase for improving the electrical conductivity of the material.

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## CLAIMS

1. A method of forming a hematite-containing protective layer on a metal-based substrate for use in a high temperature oxidising and/or corrosive environment:  
5 comprising:  
- applying onto the substrate a particle mixture comprising particles of hematite ( $\text{Fe}_2\text{O}_3$ ) and particles of:  
(a) iron metal (Fe) with a weight ratio  $\text{Fe}/\text{Fe}_2\text{O}_3$  of at least 0.3 and preferably no more than 2, in particular in the range from 0.8 to 1.4; or  
10 (b) ferrous oxide (FeO) with a weight ratio  $\text{FeO}/\text{Fe}_2\text{O}_3$  of at least 0.35 and preferably no more than 2.5, in particular in the range from 0.9 to 1.7; or  
(c) iron metal (Fe) and ferrous oxide (FeO), with  
15 weight ratios  $\text{Fe}/\text{Fe}_2\text{O}_3$  and  $\text{FeO}/\text{Fe}_2\text{O}_3$  that are in proportion with the ratios of (a) and (b);  
and  
- consolidating the applied particle mixture to form the hematite-containing protective layer by heat treating  
20 the particle mixture to:  
1) oxidise when present the iron metal (Fe) into ferrous oxide (FeO);  
2) sinter the hematite particles to form a porous sintered hematite matrix; and  
25 3) oxidise into hematite ( $\text{Fe}_2\text{O}_3$ ) the ferrous oxide (FeO), present in the mixture as such and/or in the form of the oxidised iron metal, to fill the sintered hematite matrix.
2. The method of claim 1, wherein the particle mixture  
30 further comprises particles of at least one additive selected from oxides of titanium, yttrium, ytterbium, tantalum, manganese, zinc, zirconium, cerium and nickel and/or heat-convertible precursors thereof.
3. The method of claim 2, wherein the additive(s)  
35 is/are present in the protective layer in an amount of 1 to 50 weight%, preferably 1 to 30 weight%, even more preferably 5 to 15 weight%.

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4. The method of any preceding claim, wherein the protective layer further comprises one or more metals selected from Cu, Ag, Pd, Pt, Co, Cr, Al, Ga, Ge, Hf, In, Ir, Mo, Mn, Nb, Os, Re, Rh, Ru, Se, Si, Sn, Ti, V, W, Li, Ca, Ce and Nb and oxides thereof, which are added as such and/or as precursors to the particle mixture.

5. The method of claim 4, wherein the protective layer comprises said at least one metal and/or oxide thereof, in particular copper and/or copper oxide, in a total amount of 1 to 15 weight%, preferably from 1 to 10 weight, in particular from 1 to 5 weight%.

6. The method of any preceding claim, wherein the particle mixture is made of particles that are smaller than 75 micron, preferably smaller than 50 micron, in particular from 5 to 45 micron.

7. The method of any preceding claim, wherein the metal-based substrate is metallic, a ceramic, a cermet or metallic with an integral oxide layer.

8. The method of any preceding claim, wherein the metal-based substrate comprises at least one metal selected from chromium, cobalt, hafnium, iron, molybdenum, nickel, copper, niobium, platinum, silicon, tantalum, titanium, tungsten, vanadium, yttrium and zirconium.

9. The method of claim 8, wherein the metal-based substrate comprises an alloy of iron, in particular an iron alloy containing nickel and/or cobalt.

10. The method of claim any preceding claim, comprising oxidising the surface of a metallic substrate to form an integral anchorage layer thereon to which the protective layer is bonded by sintering during heat treatment, in particular an integral layer containing an oxide of iron and/or another metal, such as nickel, that is sintered during heat treatment with iron oxide from the particle mixture.

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11. The method of any preceding claim, wherein the particle mixture is applied as a slurry onto the substrate.

12. The method of claim 11, wherein the slurry comprises  
5 an organic binder, in particular a binder selected from polyvinyl alcohol, polyvinyl acetate, polyacrylic acid, hydroxy propyl methyl cellulose, polyethylene glycol, ethylene glycol, hexanol, butyl benzyl phthalate and ammonium polymethacrylate.

10 13. The method of claim 11 or 12, wherein the slurry comprises an inorganic binder, in particular a colloid, such as a colloid selected from lithia, beryllium oxide, magnesia, alumina, silica, titania, vanadium oxide, chromium oxide, manganese oxide, iron oxide, gallium  
15 oxide, yttria, zirconia, niobium oxide, molybdenum oxide, ruthenia, indium oxide, tin oxide, tantalum oxide, tungsten oxide, thallium oxide, ceria, hafnia and thorium, and precursors thereof such as hydroxides, nitrates, acetates and formates thereof, all in the form of  
20 colloids; and/or an inorganic polymer, such as a polymer selected from lithia, beryllium oxide, alumina, silica, titania, chromium oxide, iron oxide, nickel oxide, gallium oxide, zirconia, niobium oxide, ruthenia, indium oxide, tin oxide, hafnia, tantalum oxide, ceria and  
25 thorium, and precursors thereof such as hydroxides, nitrates, acetates and formates thereof, all in the form of inorganic polymers.

14. The method of claim 13, wherein the inorganic binder  
30 is sintered during the heat treatment with an oxide of an anchorage layer which is integral with the metal-based substrate to bind the protective layer to the metal-based substrate.

15. The method of any preceding claim, wherein the particle mixture is consolidated on the substrate by heat  
35 treatment at a temperature in the range from 800° to 1400°C, in particular from 850° to 1150°C.

16. The method of any preceding claim, wherein the particle mixture is consolidated on the substrate by heat

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treatment for 1 to 48 hours, in particular for 5 to 24 hours.

17. The method of any preceding claim, wherein the particle mixture is consolidated on the substrate by heat treatment in an atmosphere containing 10 to 100 mol% O<sub>2</sub>.

18. The method of any preceding claim for manufacturing a component of a metal electrowinning cell, in particular an aluminium electrowinning cell, which during use is exposed to molten electrolyte and/or cell fumes and protected therefrom by said protective layer.

19. The method of claim 18 for manufacturing a current carrying anodic component, in particular an active anode structure or an anode stem.

20. The method of claim 18 for manufacturing a cover.

21. The method of any one of claims 18 to 20, comprising consolidating the particle mixture to form the protective layer by heat treating the cell component over the cell.

22. A method of electrowinning a metal, such as aluminium, comprising manufacturing a current-carrying anodic component protected by said protective layer as defined in claim 18, installing the anodic component in a molten electrolyte containing a dissolved salt of the metal to electrowin such as alumina, and passing an electrolysis current from the anodic component to a facing cathode in the molten electrolyte to evolve oxygen anodically and produce the metal cathodically.

23. The method of claim 22, wherein the electrolyte is a fluoride-based molten electrolyte, in particular containing fluorides of aluminium and sodium.

24. The method of claim 22 or 23, comprising maintaining the electrolyte at a temperature in the range from 800° to 960°C, in particular from 880° to 940°C.

25. The method of any one of claims 22 to 24, comprising maintaining in the electrolyte, particularly adjacent the



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anodic component, an alumina concentration which is at or close to saturation.

26. The method of any one of claims 22 to 25, comprising maintaining an amount of iron species in the electrolyte to inhibit dissolution of the protective layer of the anodic component.

27. A method of electrowinning a metal, such as aluminium, comprising manufacturing a cover protected by said protective layer as defined in claim 19, placing the cover over a metal electrowinning cell trough containing a molten electrolyte in which a salt of the metal to electrowin is dissolved, passing an electrolysis current in the molten electrolyte to evolve oxygen anodically and the metal cathodically, and confining electrolyte vapours and evolved oxygen within the cell trough by means of the protective layer of the cover.

28. A hematite-containing protective layer on a metal-based substrate for use in a high temperature oxidising and/or corrosive environment, producible by the method of any one of claims 1 to 22, which is dense and at least substantially crack-free.

29. A cell for the electrowinning of a metal, such as aluminium, having at least one component that comprises a metal-based substrate covered with a hematite-containing protective layer as defined in claim 28.

30. A method of forming a hematite-containing body for use in a high temperature oxidising and/or corrosive environment: comprising:

- providing a particle mixture comprising particles of hematite ( $\text{Fe}_2\text{O}_3$ ) and particles of:
  - (a) iron metal (Fe) with a weight ratio  $\text{Fe}/\text{Fe}_2\text{O}_3$  of at least 0.3 and preferably no more than 2, in particular in the range from 0.8 to 1.4; or
  - (b) ferrous oxide ( $\text{FeO}$ ) with a weight ratio  $\text{FeO}/\text{Fe}_2\text{O}_3$  of at least 0.35 and preferably no more than 2.5, in particular in the range from 0.9 to 1.7; or

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- (c) iron metal (Fe) and ferrous oxide (FeO), with weight ratios Fe/Fe<sub>2</sub>O<sub>3</sub> and FeO/Fe<sub>2</sub>O<sub>3</sub> that are in proportion with the ratios of (a) and (b);
- shaping the particle mixture into the body;
- 5 and
- consolidating the body by heat treating the particle mixture to:
- 1) oxidise when present the iron metal (Fe) into ferrous oxide (FeO);
  - 10 2) sinter the hematite particles to form a porous sintered hematite matrix; and
  - 3) oxidise into hematite (Fe<sub>2</sub>O<sub>3</sub>) the ferrous oxide (FeO), present in the mixture as such and/or in the form of the oxidised iron metal, to fill the
  - 15 sintered hematite matrix.
31. The method of claim 30, incorporating any of the features of claims 2 to 6 and/or wherein the particle mixture is provided in a slurry and consolidated as defined in any one of claims 12 to 13 or 15 to 17.
- 20 32. The method of claim 30 or 31, for manufacturing a component as defined in claims 18 to 20.

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## ABSTRACT

A method of forming a dense and crack-free hematite-containing protective layer on a metal-based substrate for use in a high temperature oxidising and/or corrosive environment comprises: (I) applying onto the substrate a particle mixture comprising particles of hematite ( $\text{Fe}_2\text{O}_3$ ) and particles of: (a) iron metal (Fe) with a weight ratio  $\text{Fe}/\text{Fe}_2\text{O}_3$  of at least 0.3 and preferably below 2, in particular in the range from 0.8 to 1.4; or (b) ferrous oxide (FeO) with a weight ratio  $\text{FeO}/\text{Fe}_2\text{O}_3$  of at least 0.35 and preferably below 2.5, in particular in the range from 0.9 to 1.7; and (II) consolidating the applied particle mixture to form the hematite-containing protective layer by heat treating the particle mixture to: 1) sinter the hematite particles to form a porous sintered hematite matrix; and 2) oxidise into hematite ( $\text{Fe}_2\text{O}_3$ ) the iron metal (Fe) and the ferrous oxide (FeO) to fill the sintered hematite matrix. The mechanical, electrical and electrochemical properties of the protective layer can be improved by using additives, such as oxides of titanium, zirconium and/or copper. Typically the protected substrate can be used in a cell for the electrowinning of a metal such as aluminium.